

6. *Summary.*

(1) The specific heats of aqueous hydrofluoric acid of different concentrations have been determined and the results recorded in Table I.

(2) The heats of solution of quartz and silica glass in aqueous hydrofluoric acid have been determined (Table II), and the difference, which represents the heat of crystallisation of quartz at the ordinary temperature, is found to be equal to 6.95 Kgrm.-cals.

(3) From determinations of the heats of solution (Table III) it has been shown that grinding affects the crystalline material, which is partially converted into the vitreous state.

(4) The latent heat of crystallisation of quartz has been calculated at higher temperatures, and it is shown that near the melting-point the heat of crystallisation of quartz is very nearly equal to that at the air temperature.

My best thanks are due to Dr. M. W. Travers, F.R.S., at whose suggestion the work was undertaken, for the help I have received from him. I must also thank Prof. F. G. Donnan, F.R.S., for affording me the facilities in carrying out the work, and Mr. W. E. Garner, M.Sc., for the use of the platinum-iridium resistance.

---

*The Properties and Molecular Structure of Thin Films.*

Part III.—*Expanded Films.*

By N. K. ADAM, M.A., University of Sheffield.

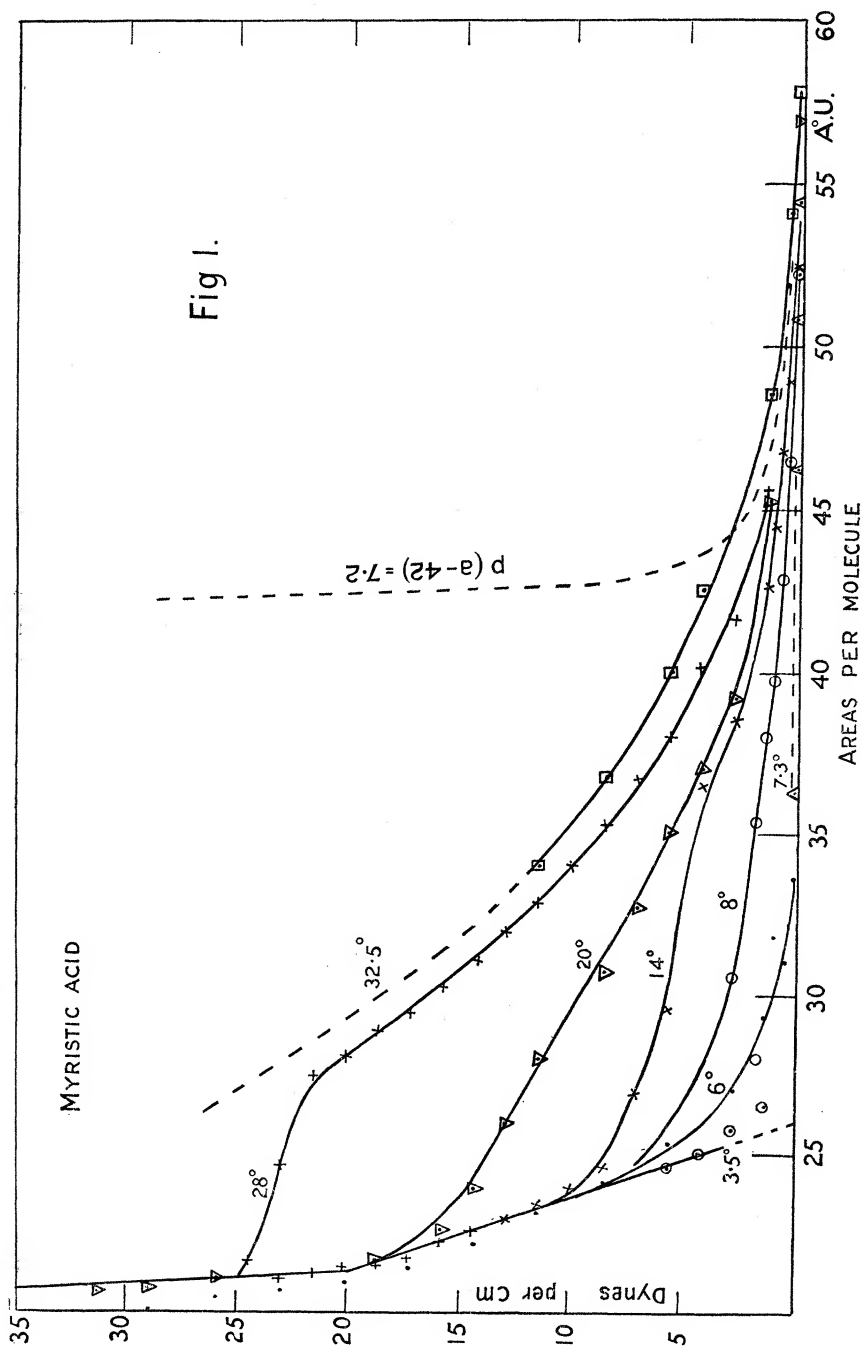
(Communicated by W. B. Hardy, Sec. R.S. Received May 4, 1922.)

1. *Expansion of Films of the Fatty Acids on Dilute HCl.*

In the previous paper an account was given of the properties of the films over a range of temperature low enough for it to be permissible to regard the molecules as in direct contact over the whole area, except perhaps for a very slight tendency to separate under the lowest compressions; this tendency being perhaps analogous to vapour pressure. The films in this condensed condition were either solid or liquid. Within the accuracy of my experiments, the mechanical properties of condensed films were independent of temperature.

The present paper describes the phenomena observed above this range of temperature. At a certain temperature all the films expand along the surface, the actual temperature of expansion depending both on the nature of the substance in the film, and on the composition of the solution. The phenomena exhibited by films of the fatty acids on dilute HCl have been the most thoroughly investigated, and will be first described.

Fig. 1 gives the compression curves of myristic acid ( $C_{14}$ ) at various temperatures,  $3.5^\circ$ ,  $6^\circ$ ,  $7.3^\circ$ ,  $8^\circ$ ,  $14^\circ$ ,  $20^\circ$ ,  $28^\circ$ , and  $32.5^\circ$ . Those at  $3.5^\circ$  and  $28^\circ$



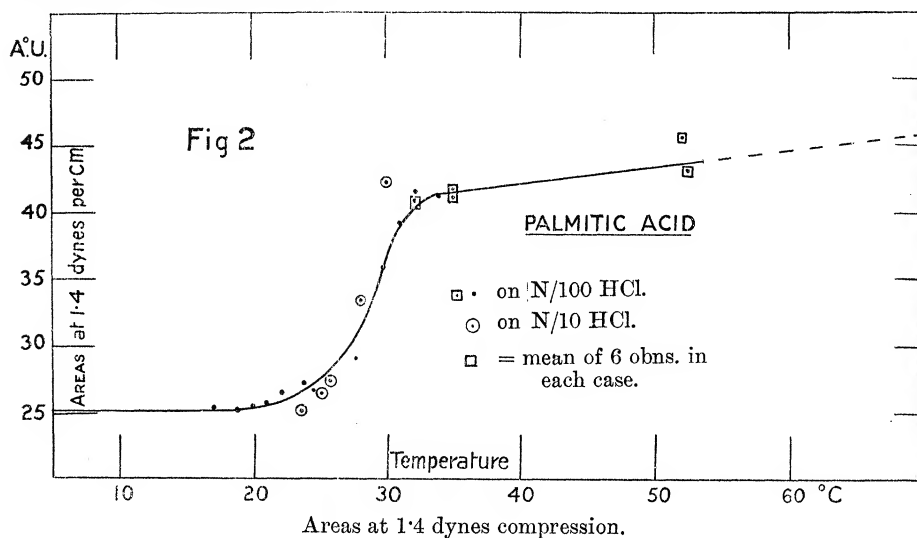
were done on N/10 HCl, the remainder on N/100. There appeared to be a slightly greater extension of the films on the N/100 than on the N/10, for a few degrees below  $10^{\circ}$ , but the difference was almost within the experimental error. The temperatures are probably correct to  $0.5^{\circ}$ . The curve at  $3.5^{\circ}$  is practically the same as the typical curve of compression of condensed films of fatty acids on this solution (Part II, fig. 2, III). At  $6^{\circ}$  a slight extension appears, below 10 dynes per centimetre compression, but at 35 Å.U. area the "vapour pressure," referred to in the last paragraph of Part II, was still below 0.29 dynes per centimetre. At  $7.3^{\circ}$ , in one experiment, the "vapour pressure" was found to be almost exactly 0.29 dynes per centimetre; it was possible to alter the area over the range indicated by the dotted line with scarcely any movement of the balance float. At  $8^{\circ}$  the "vapour pressure" was nearly five times as great. At  $14^{\circ}$  and higher temperatures, the lowest portion of the curves somewhat resembles a hyperbola, but at a fairly definite point the curves become of less steep slope and pass rapidly to the left (the area of the film decreasing), rising steeply again only when nearing the typical condensed curve. There are thus two points of inflexion in the curves, the second being on a part of fairly gentle slope. Many experiments have been done at intermediate temperatures, which showed that the compression required to reach this second point of inflexion rises steadily with increasing temperature, curves being distinguishable by this ordinate when only about  $1^{\circ}$  C. apart. These curves occupy positions intermediate between those shown in the figure. Finally, when the temperature rises more than about  $25^{\circ}$  above that at which the first divergence from the condensed curve is perceptible, the inflexions are no longer visible on the curves, since the compressions which would be required to reach them are so great that collapse of the films has already occurred.

No appreciable hysteresis has been observed in any experiment upon expanded films.

All the fatty acids mentioned in Part II have been examined on dilute HCl, except cerotic, and all show substantially the same phenomena, though at different temperatures. In the cases of oleic, lauric, and tridecyllic acids, only the more or less hyperbolic part of the curves could be traced experimentally, because the whole or the main part of the transitional range of temperature was below  $0^{\circ}$  C. Erucic and elaidic acids also gave films not completely condensed at the lowest temperatures which could be reached, though a large part of the transitional region was examined.

In fig. 2 the area of the film is plotted against the temperature under a small compression of 1.4 dynes per centimetre, for palmitic acid. There is only a small transition range of temperature between the upper slightly

sloped line of the expanded film, and the lower horizontal line of the condensed film, the change being completed in about  $13^{\circ}\text{C}$ . The points from which the line has been drawn were determined on  $\text{N}/100\text{ HCl}$ ; a few ringed points obtained on  $\text{N}/10$  acid are added, which indicate that the expansion is, if anything, more sudden on this solution, but occurs at the same mean temperature. Similar curves have been obtained for all the fatty acids on this solution, except where the temperature of expansion was below  $5^{\circ}$ . All have the same S shape, the interval of temperature not being greater in any case than for palmitic acid.



The coefficient of thermal expansion of the expanded films would, from the analogy with a gas to be developed later, be expected to be the same as that of a perfect gas. Unfortunately, the difficulties of experiment are too great to make a satisfactory measurement of this quantity. In fig. 2, the upper line has been drawn with a slope which corresponds to this coefficient of thermal expansion. The points in rectangles have been determined with the greatest care, but they do no more than confirm the order of magnitude of this slope. Above about  $50^{\circ}$  accurate measurements with palmitic acid become impossible on account of solubility. Neither has it been found possible to carry accurate measurements of the expanded areas of other substances to temperatures sufficiently above the expansion temperature to give a better verification of the coefficient of increase of the expanded area with temperature. Referring to fig. 1, an indication is given that there is some lateral shifting of the hyperbolic part of the curves as a whole to the right as the temperature rises (although probably a part of the difference between the positions of the curves

at 28° and 32.5° is fortuitous); and I have obtained similar results on other films also where sufficiently accurate experiments have been done. This effect of temperature on the expanded films is therefore existent at all compressions, although the data are not accurate enough to give a measure of its amount.

The influence of the length of the hydrocarbon chains in the series of saturated acids on the temperatures of expansion was most interesting, a steady rise being observed with increasing molecular weight. The data are collected in Table I. It will be noticed that there is no difference between the even and odd members of the series, such as is well known in the melting points of the crystals.

A slight difference in the areas to which expansion takes place also exists between acids of different length of chain, and is very probably due to the attraction between the chains being greater in the long chains than the short, so that there is a greater correction to be subtracted from the area, analogous to the  $a/v^2$  correction in Van der Waals' equation.

The unsaturated acids expand at lower temperatures than the saturated acid with the same number of carbon atoms. The effect of a double bond in the  $\alpha\beta$  position on this property is much the same as that of shortening the chain by two carbon atoms. For double bonds in the middle of the chain the stereochemical configuration is very important, the form with the lower melting point (oleic and erucic) expanding some 70° lower than the corresponding saturated acid, while the other isomer expands only about 40°–45° lower. These differences are probably a consequence of different lateral attraction of the chains, a cause which may also be responsible for the slight differences in the areas to which the films of these substances expand.

The data in Table I were determined at the arbitrary small compression of 1.4 dynes per centimetre, which is the lowest compression at which accurate measures of area have been obtained. The temperature of half-expansion is the temperature at which the area of the film was the arithmetic mean between the areas of the completely expanded film and of the condensed film. This temperature is better defined, owing to the shape of the curve, than the temperature of commencement or of completion of expansion. The areas for the saturated acids have been determined with the greatest care, in order to establish whether the expanded area really varied with molecular weight in this series or not; probably, except for the acids with the two longest chains, the error is well within one unit. Each of the figures in the fourth column up to C<sub>21</sub> is the mean of six good measurements. The areas given have been determined at temperatures not more than 10° above that at which expansion becomes complete under 1.4 dynes, in order to minimise errors due to

solubility of the molecules; but control experiments giving closely agreeing results were done in most cases at higher temperatures, in order to make sure that the area measured was really that of a fully expanded film.

In order to compare the areas for different members of the series, they have been corrected to 0°, using the coefficient of thermal expansion of a gas. Of course, at this temperature most of the films are not, in fact, expanded. Sufficient measurements have, however, been made at the same temperature on members of the series differing by up to three carbon atoms, to make sure that the gradual decrease in area occupied with increasing molecular weight is not due to the correction being erroneous.

Table I.—Expansion of Films of Fatty Acids on dilute HCl, under 1.4 dynes per cm. compression.

Acid.	No. of carbon atoms.	Temperature of half expansion.	Area of expanded film.	Temperature of determination of area.	Area corrected to 0° C. (mean).
Lauric .....	12	below 0	48.2	16.5	45.1
Tridecylic .....	13	below 0	47	14	42.5
Myristic .....	14	9	43.6	11.5	40.6
Pentadecylic .....	15	19.5	43.5	18	38.8
Palmitic .....	16	28.5	43.9	24	36.8
Margaric .....	17	37.5	42.0	25.3	36.6
Stearic .....	18	46	42.2	22.5	36.1
Heneicosoic .....	21	65.5	41.3	35	(36.4)
Behenic .....	22	72.5	41.7	34.5	(36.0)
Iso-oleic .....	18	25	42.6	41	(40.8)
Oleic .....	18	below 0	41.7	43.5	(50.5)
Elaidic .....	18	— 0.5*	42.9	52.5	(45.4)
Erucic .....	22	4.5	43.2	53	(45.4)
Brassicic .....	22	34	(46.0)	77	(39.2)
			(47.5)	80	
			(45.9)	75	
			(46)	35	
			(52.5)	10	
			(47)	10	
			(47)	10	
			(45)	40	

Figures in brackets are less accurate than the others, but are probably within two units of the correct value.

\* For elaidic acid the point of half expansion is not directly observable; but comparison of the curves similar to those in fig. 1, obtained for erucic and elaidic acid, showed that corresponding stages of expansion are reached 5° lower with elaidic than with erucic acid.

## 2. Expansion of Fatty Acids on other Solutions.

Some of the acids have been examined upon distilled water, on a phosphate solution of  $\text{P}_{\text{H}}6$ , and on N/10 soda. These results have not been obtained as accurately as the preceding, but they show several points of interest.

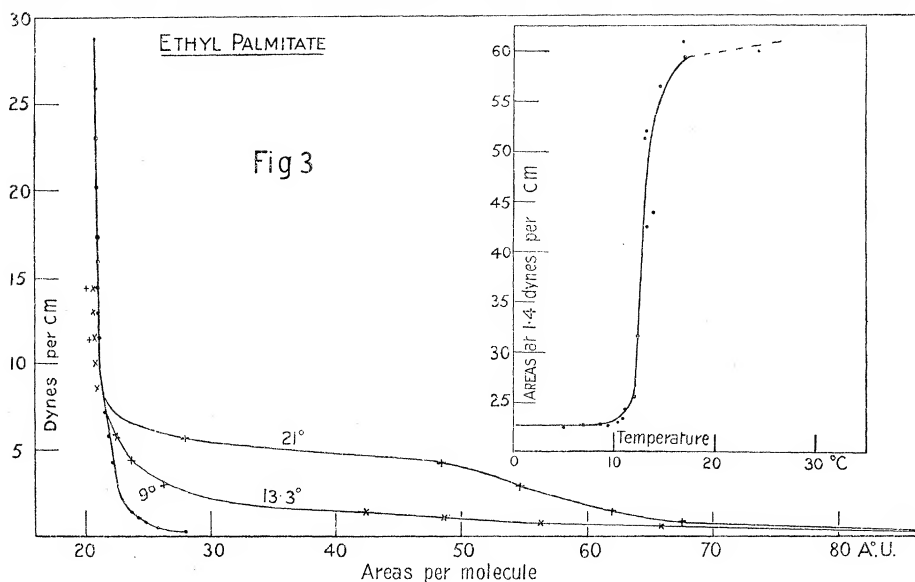
On distilled water, and on the P<sub>H</sub>6 solution, the temperatures of expansion were not quite definite, but depended on the time the solution had been in the trough, this effect being no doubt connected with the other effects of the age of the solution described in Part II. The temperatures varied from about 5° to 15° higher than the expansion temperatures for the same acids on HCl. The lowest temperatures were obtained on the fresh solution, the highest after standing some time in the trough. The areas to which expansion extended were very slightly less than on HCl.

On N/10 NaOH solution the measurements of area were probably slightly smaller than the true values, as there was some solution; but this was surprisingly slow with acids higher than palmitic. The expansion was the largest yet found, being to about 120 Å.U. at 1.4 dynes per centimetre. The temperatures of expansion were about 30° lower than on N/100 HCl.

On all these solutions the effect of increasing the length of the chain by one carbon atom was to raise the temperature of expansion by exactly the same amount as on HCl, *i.e.*, about 10° in the region of 0°, and about 8.5° near 40°.

### 3. Expansion Phenomena with other Substances.

The curves of compression for ethyl palmitate at three temperatures are given in fig. 3, and also the variation of area under 1.4 dynes per centimetre



compression with temperature. The expansion is to greater areas than with the acids on neutral and acid solutions, and the curves at temperatures in the transition region are flatter, but the main points of figs. 1 and 2 are

reproduced. The behaviour of ethyl palmitate was exactly the same in respect of temperature of expansion and area on HCl as on water. Very similar expanded curves were obtained on methyl, propyl, butyl and octyl palmitates. Methyl palmitate requires a higher temperature for expansion than ethyl; propyl and the esters of higher alcohols up to octyl, however, are more easily expanded, and condensed films of these substances probably only exist below 0°. There is an interval between the temperature of expansion of ethyl palmitate and ethyl stearate almost equal to that between the expansion temperatures of the two fatty acids, whose chains differ in length by two carbon atoms, and whose temperatures of expansion lie in the same region.

Tripalmitin and tristearin on distilled water expand at temperatures which differ by considerably less than the usual difference between films of substances whose chains differ in length by two carbon atoms. This is the only exception yet found to the rule that adding one carbon atom to the chain raises the temperature of expansion by the same amount, whatever the nature of the head or the length of the chain; and this anomaly is no doubt connected with the fact that the films of these substances break up on expansion, not into single chains, but into groups of three. Table II gives the collected results.

Table II.—Expansion of various Substances on Distilled Water, under 1.4 dynes per cm. compression.

Substance.	No. of carbon atoms in hydro-carbon chain.	Temperature of half expansion.	Area of expanded film corrected to 0° C.
Methyl palmitate .....	16	27.5	(46)*
Ethyl „ .....	16	13	55
Propyl „ .....	16	(below 5)	(76)
n-Butyl „ .....	16	(below 5)	(74)
n-Octyl „ .....	16	(below 5)	(76)
Ethyl stearate .....	18	33	45.4
Tripalmitin .....	16	48	29.5
Tristearin .....	18	57	29.9
Cetyl alcohol.....	16	49	(30.8)†
Heptadecyl urea .....	17	55	33
Octadecyl urea .....	18	62.5	33.7
Stearic amide.....	18	58	32.2
Stearic nitrile .....	17	26	36.4
Octadecylamine hydrochloride	18	(26.5)	46

\* Methyl palmitate dissolved at the temperature of this measurement fast enough to cause slight uncertainty.

† Also rendered probably too small by solution.



*4. Comparison between the Expanded Films and Gases.*

The only theory of the expanded state which seems at all probable is that, in the process of expansion, the molecules become separated from each other and move about independently on the surface. In this condition the film resembles a gas, and, since the molecules are confined to the surface by reason of their insolubility, the barriers on the surface take the place of the walls of the vessel confining the gas. The pressure on the barriers thus differs in the case of the expanded films from the pressure exerted by the condensed films, in being exerted by a series of impacts rather than by a steady thrust. There is therefore on the surface, in the expanded films, a considerable space not actually covered by the molecules, at any instant.

The very close resemblance between the "isothermals" in figs. 1 and 3 and the isothermals of a vapour near the critical point is obvious, and is strong evidence in support of this way of regarding the films. The fully expanded films are not rectangular hyperbolas; however their departure from this form is not evidence against the view that the films are analogous to gases, but is a measure of the corrections to the simple gas laws which must be applied to the films, for the area occupied on the surface by the molecules, and for their mutual lateral attractions. That these corrections will need to be rather larger than in the case of gases is natural, since the difference in area between the condensed and the expanded films is much less than the difference between the volumes of most substances in the liquid and vapour states.

There is, however, an important point of difference from a gas. In a gas the molecules which exert the pressure are the only ones in the enclosure, and the only collisions they experience are those with the walls and with other molecules, which will later themselves strike the boundaries and exert pressure. The film molecules, however, are continually subject to forces from the molecules of the underlying solution, both attractions and repulsions; and these underlying molecules do not themselves at any time exert tangential forces on the boundaries. It is these forces which probably mainly determine the motions of the film molecules. The intensity of these forces from the molecules of water and substances dissolved therein will depend upon the composition of the solution, and upon the chemical nature of the heads of the film molecules; it will also increase with the temperature. A fuller understanding of the properties of the expanded films should therefore be of service in shedding light on the problem of the nature of the forces between solvent and dissolved molecules.

5. *Nature of the Process of Disruption of Condensed Films, or "Vaporisation."*

The attractive forces which hold the condensed films together had to be considered even in the discussion of condensed films. It was stated at the beginning of Part II that the theory would be developed on the assumption that there was no tangential surface force on the films *as a whole* from the water molecules. When, however, the individual molecules of a condensed film are considered, the random tangential movements of the molecules of water (and substances dissolved in it) must impart similar movements to the film molecules; the resultant of which, since the motions are equally distributed in all directions, must vanish when an area large enough is considered. Such forces will tend to separate the film molecules from one another and to cause expansion when they reach sufficient intensity to overcome the forces of lateral adhesion between the film molecules. The legitimacy of neglecting the tangential forces and motions when a large area is considered is evident; in the precisely similar case of Brownian movement, the particles show no movement if large enough, because the number of collisions with moving molecules is so great that their resultant in any direction practically vanishes, while the smaller particles receiving fewer impacts are able to discriminate between the random motions of the molecules.

The influence of the contribution made to the lateral attractions by the hydrocarbon chains is obvious when the expansion temperatures of successive members of the homologous series are considered. The addition of one  $\text{CH}_2$  group to the molecule makes a definite rise in the expansion temperature of the film.

It is most probable, however, that the polar heads of the molecules also contribute considerably towards the lateral cohesion. In the preceding paper it has been shown that the heads of the molecules are an important factor in the solidity or otherwise of the films, so that cohesive forces are to be presumed between them. Also the same polar groups must have a considerable attraction for one another in short chain compounds, since these possess considerable cohesion. It is difficult, however, at present to decide what proportion of the lateral attraction must be ascribed to the heads and what to the chains.

6. *Corrections to the Expanded Films for the Area Occupied by the Molecules and the Lateral Attraction.*

For a perfect gaseous film the equation of the isothermals would be  $pA = KT$ ,  $A$  being the area and  $p$  the compression in dynes per centimetre

This equation does not fit the curve in fig. 1 at  $32.6^\circ$ , and in order to obtain the right correction it will be necessary to carry the calculations of the correction required from the area occupied by the molecules to much greater accuracy than is done in Van der Waals' equation. By repeating the calculations in Jeans' 'Dynamical Theory of Gases,' 1921 edition, pp. 126-127, substituting areas for volumes, it is easily seen that the correction to be subtracted from the area of the films, corresponding to Van der Waals' " $b$ ," is here twice the area of the molecules, instead of four times as in the case of gases. The total area of a film composed of closely packed chains has been found to be  $21.0 \text{ \AA.U.}$  per molecule; the dotted curve in fig. 1 is that of  $p(A-42) = 7.2$ , but the actual curves pass very much to the left of this. It is well known, however, that the " $b$ " correction to gases is too large at high condensations, so this lack of agreement is not evidence against the more or less independent motion of the molecules in the expanded films and their analogy with gases. It should be pointed out also that although the total area occupied by a film of close packed chains or heads is known, the manner of packing is not, nor whether the collisions in the expanded state take place between the heads or the chains. There is, therefore, some uncertainty as to the area of a single molecule which should be taken into account in considering the correction just discussed.

It does not seem worth while to attempt a quantitative correction for the lateral attractions until the large correction for the area covered by the molecules has been carried to much greater accuracy. An effect which is probably due to this attraction, namely, that the molecules with longer chains expand to somewhat smaller areas, has already been mentioned.

#### 7. *Difficulties attending any Conceptions of the Expanded Films other than the Analogy with Gases.*

On the explanation given there are spaces not covered by the molecules. The expanded films are therefore "one molecule thick," though not in quite the same sense as the condensed films. It does not seem possible to account for the phenomena on any explanation in which the molecules are assumed touching all over the area.

The increase of area cannot be due to the molecules lying flat on the surface. The area even at very low compressions is often not more than  $50 \text{ \AA.U.}$  Since the cross-section of a molecule of stearic acid is  $21.0 \text{ \AA.U.}$ , assuming a circular cross-section, its diameter must be  $5.2 \text{ \AA.U.}$ , and therefore the minimum area it could occupy when lying flat would be  $109 \text{ \AA.U.}$ , which is much too large. Moreover, if the expanded state were due to some only of

the molecules lying flat, the area per molecule would probably increase with the length of the chain; whereas experiment shows, on the contrary, that the area is somewhat less for long molecules than for short.

It might also be suggested that the molecules are vertical and in contact everywhere in the film, but are subject at higher temperatures to such violent thermal oscillations that they require a larger area. It would be exceedingly difficult to explain the sudden nature of the expansion on this hypothesis; a steady increase in area with rising temperature would rather be expected, instead of the rapid rise in figs. 2 and 3. To explain the discontinuity the process must be analogous to a transition from one form to another, or change of state; and the only common change of state in other states of matter which is attended with large change in volume is that from liquid or solid to gas. Therefore, the surface change of state which causes the expansion of the films must be analogous to the vaporisation of a condensed substance.

Finally on any theory of the expanded films which could come in this class, it would be necessary to give an explanation of the striking resemblance between the "isothermals" of the films and those of a vapour near the critical point. The oscillations in the chains would have to be of a very extraordinary kind for their amplitudes to be diminished by increasing compression in the manner required to fit these curves.

#### 8. *The Orientation of the Separated Molecules in the Expanded Films.*

Exact information as to the area covered by the molecules in the separated condition can only be obtained by the evaluation of the corrections for the area covered and the lateral attractions between molecules, and comparison with the compression curves of a fully expanded film. As the evaluation has not yet been carried out, only the order of magnitude of the area covered can be obtained. Since the curve of the equation  $p(A-42) = 7.2$ , which is plotted in fig. 1, is so far to the right of the experimental curves, it does not seem probable that the molecules in the expanded film can actually cover an area much greater than 21.0 Å.U., even when separated from each other; therefore they must probably be vertically arranged.

Other considerations point in the same direction. If the molecules were much inclined to lie flat on the surface, the "b" correction would be much greater for long molecules than for short. This is not the case experimentally, since expanded films of long molecules actually occupy smaller areas than those of short. It is very difficult to account for the approximate equality of the "b" correction when the molecules are of widely differing lengths unless the orientation is substantially vertical.

*9. The Orientation of Unsaturated Acids.*

Langmuir suggested originally, that the tendency of oleic acid to occupy on the surface an area about double that of palmitic was due to the double linkage half-way up the chain being itself attracted to the water, and therefore providing a second point of attachment. The expanded films of oleic and the other unsaturated acids, however, have compression curves very much like those of the saturated acids, such differences as exist being very likely due to the correction for the lateral attraction between molecules being somewhat less for these substances than for the saturated acids. Therefore the "*b*" corrections are of the same order of magnitude, and it follows from the arguments in the preceding paragraph that the orientation of these substances also is practically vertical. The argument, therefore, that the molecules double up, so that the unsaturated linkages in the middle of the chains are in contact with the water, entirely loses its foundation; and the reason why it was at first advanced is seen to be that the distinction between condensed and expanded films was not then clearly recognised.

In a letter to 'Nature' (Part II, Reference 4) I pointed out that on the assumption of the molecules bending so as to bring the double linkage into contact with the water, the greater ease with which oleic rather than elaidic occupied the larger area was evidence in favour of the "cis" configuration for oleic and the "trans" for elaidic acid. Since the assumption is now proved incorrect, the films do not afford independent evidence at present as to the stereochemical configuration of these substances. It can only be said that the lateral attraction of the oleic molecules is less than that of the elaidic, and similarly the attraction of the erucic molecules is less than that of brassidic. This fact, if the considerations in the next paragraph are correct, is connected with the relationships between the melting points of the crystals of the isomers.

*10. Evidence available, from the Study of the Films, and the Melting Points of the Crystals, as to the Crystal Structure of Fatty Acids and their Esters.*

In Table III are given the melting points of the esters of palmitic acid with various alcohols. As the size of the alcoholic group increases, the melting point first diminishes very rapidly from that of the acid; then it is lowered more slowly, and finally begins to rise and continues to do so up to the highest member of which there is a record. The melting points from propyl to octyl palmitates are determined on my preparations, no determinations being apparently recorded previously. These determinations

are accurate enough for the present argument, but should not be taken as standard values, since no analyses have been done of these compounds, and although the alcohols were probably of high purity, in one or two instances they may have been insufficiently dehydrated.

There are two other important relationships; the melting points of the acids and esters rise with increase in the length of the hydrocarbon chains; and the melting points of the acids and esters with an even number of carbon atoms in the molecule lie on one regularly ascending series, the odd members lying on another with melting points about 7° lower.

In the films the explanation of the steady increase in the expansion temperature with length of chain was shown to be due to the chains lying side by side, and attracting one another laterally; it is probable, therefore, that in the crystals also the chains lie alongside, over some considerable part

Table III.—Palmitic Acid and its Esters.

Substance.	Melting point of crystal.	Temperature of half expansion on dilute HCl.
	°	°
Free acid .....	62·5	28·5
Methyl ester .....	30	27·5
Ethyl „ .....	25·5	13
<i>n</i> -Propyl „ .....	15-16	below 5
<i>n</i> -Butyl „ .....	13-14	below 5
iso-Butyl „ .....	19-20	Unknown.
iso-Amyl „ .....	11-12	
<i>n</i> -Octyl „ .....	24-25	below 5
<i>n</i> -Dodecyl ester* .....	41	Unknown.
<i>n</i> -Tetradecyl ester.....	48	„
Cetyl ester .....	53-54	„
<i>n</i> -Octadecyl ester .....	59	„

\* The last four determinations are taken from Krafft, 'Ber. Deutsch. Chem. Ges.,' vol. 16, p. 3017.

of their length. The influence of the size of the alcoholic group on the crystal melting probably indicates that there is a second force of great importance concerned in holding the crystal together, namely the attraction of the polar groups for one another; this is paralleled in the films by the attraction of the polar groups for the water as well as for one another.\* This attraction between polar groups appears to be diminished by the introduction of small esterifying groups, such as ethyl or methyl. When the hydrocarbon chain of the alcoholic part of the molecule exceeds about seven carbons in length, probably these long chains supply a second stabilising force.

\* The latter part of this section was re-written June 29.

These facts form some guide as to the possible arrangements of the molecules within the crystals; it is assumed that the attractions do not extend to distances much greater than the interval between adjacent atoms, or, at any rate, are much more intense within these distances than beyond. In the acids, and the lower esters, the hydrocarbon chains must lie side by side, and the oxygen-containing groups of several molecules also must lie close together. A possible arrangement would be for the polar groups of a number of molecules to be arranged together in a clump, as a core surrounded by a shell of hydrocarbon chains. A perhaps more probable arrangement has been suggested to me in conversation by Prof. Lowry, F.R.S., that the molecules are in parallel layers with the hydrocarbon chains alongside and polar groups in each layer all in the same direction; the polar groups of one layer in contact with those of the next, and the hydrocarbon ends touching the corresponding ends of the molecules in the next layer on the other side. The latter arrangement admits of the insertion of alcoholic hydrocarbon chains of any length in the esters, without radically altering the arrangement, in the same line as the chains of the acidic part of the molecules; the former would require a fundamental re-arrangement at about the octyl ester.

11. *The Independence of the Properties of Solubility in the Underlying Solution and Expansion along the Surface.*

In his original paper (Part II, reference 5, p. 1889) Langmuir compared the layer of concentrated solute or adsorbed film in the surface of solutions with a gas, showing that the adsorbed molecules may obey approximately a law  $pA = KT$  in the surface. He also showed that the surface monomolecular films of palmitic acid, or condensed films, possess an immeasurably small "vapour pressure" in the surface. In contrasting the two kinds of film, the insoluble acid films which are also condensed, and the "gaseous" films of adsorbed substances, he said: "The smallness of this (vapour) pressure for the higher fatty acids must be due to attractive forces between the molecules powerful enough to prevent their separation. These same forces tend to prevent the film from evaporating from the surface into the vapour phase, and from going into solution in the water. There are thus intimate relationships between the lowering of surface tension produced by fatty acids and the vapour pressures and solubilities of these substances."

This way of stating the relationships gives the impression that it is the lateral adhesion between the molecules which prevents the films dissolving, and that an isolated molecule on the surface would dissolve very rapidly. I do not think there is any *a priori* reason for taking this view, although, no

doubt, a long hydrocarbon chain tends both to diminish solubility and to cause the molecules to adhere together on the surface. My experiments have shown a certain amount of independence between the tendency to dissolve and to separate laterally on the surface. Thus films of palmitic acid remain practically insoluble for some 20° above the temperature of expansion, but with cetyl alcohol, the solubility is marked some distance below the temperature of expansion.

It does not seem legitimate to state, *a priori*, what will be the relation between the tendency to dissolve and the tendency to expand; but as both these quantities are now capable of independent measurement, I hope to obtain some results on this problem in the near future.

---

*Diffusion and Intertraction.*

By C. G. SCHONEBOOM.

(Communicated by Prof. Sir E. Rutherford, F.R.S. Received May 24, 1922.)

(From the Laboratory of the Institute of Pathology and Research, St. Mary's Hospital London.)

The starting-point of this investigation was the phenomenon which Sir Almroth Wright described in the 'Proceedings of the Royal Society,' Series B, vol. 92. The original experiment is conducted by putting 5 or 8 per cent. NaCl in a test-tube or flat glass cell and allowing some blood serum to run slowly on the top of the NaCl. As soon as the fluids are brought into contact, a mass movement is started, the upper fluid being carried down into the lower and the lower into the upper. The characteristic appearances so produced are well described by the terms intertraction or pseudopodial interpenetration. By colouring the serum with a trace of some dyestuff (*e.g.*, eosin) the intertraction phenomenon is easier to follow; or by having a layer of tannic acid or sulpho-salicylic acid in NaCl solution on the bottom, one sees after a short time (some minutes) a heavy precipitate in the lower interface.

This system, serum on NaCl solution, presents a typical example of the intertraction phenomenon, as will be described in the following experiments, in so far that in the case of serum and NaCl solution both fluids are, so to speak, active and penetrate each other quickly, so that after some time (10 to 30 minutes) the contents of the vessel are a homogeneous mixture, as can readily be seen if eosin be used in the serum. This result, the homogeneous